PC Codes: 128825, 109702, 128831, 097805, 109303, 127901, 128897, ~~109101~~ 109701 MRID 48638501
Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin & Permethrin
Pyrethroid Working Group (PWG) EPA Company Code 64977

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Data Requirement: EPA Guideline: Non-guideline, 835.6100, 835.6200
OECD Data Point: IIA 4.9 Other/special studies

Test material:
Common names: Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin
Chemical name: Refer to the Attachment II
IUPAC: Refer to the Attachment II

José Luis Meléndez 10/24/2011

Primary Reviewer: José L. Meléndez, Chemist

Reuben Baris 11/01/2011

Secondary Reviewer: Reuben Baris, Environmental Scientist
EFED's Pyrethroid Review Team Representative

ANALYTICAL METHOD: Willoh, J.M., 2010, "Validation of Morse Laboratories, LLC Analytical Method (METH-201): "Determination of residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater (Influent and Effluent)," Dated September 30, 2010. Morse Labs Project No.: ML10-1602-PWG. Date of the Report December 3, 2010. Unpublished study performed by Morse Laboratories, LLC, and submitted by the Pyrethroid Working Group (PWG), 200 pp. (MRID 48638501)

INDEPENDENT LABORATORY VALIDATION: Not Available

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

EXECUTIVE SUMMARY

This method is designed for the quantitative determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in wastewater influents and effluent samples from Publicly Owned Treatment Works (POTWs). The method was created by Morse Laboratories, LLC. The Agency found that this method does not meet the criteria for a scientifically valid method and only provides limited information for the analytes in wastewater influents and effluent samples. The major problem of the method is that it does not have a true independent laboratory validation. LODs and LOQs are highly uncertain because only two matrix blank samples were tested for each analyte.

Method Summary: Samples were taken from a POTW facility in Suffern, NY. Influent samples were collected after bar screening and a comminutor (*i.e.*, pulverizes solids), but prior to grit removal, resulting in removal of large objects from the wastewater. Effluent samples were collected after primary settling, trickling filter biological treatment with secondary clarification, activated sludge biological treatment, final settling through integral clarifiers and ultraviolet disinfection. The sample residues are extracted by first adding methanol to the wastewater sample, then partitioning the mixture twice with hexane. The combined hexane layers are passed through sodium sulfate, evaporated to dryness and re-dissolved in hexane. The hexane sample is subjected to a silica solid phase extraction (SPE) cleanup procedure. The residue is determined by gas chromatography with mass selective detection using negative chemical ionization (GC-MSD/NCI). Based upon the study, uncertain estimates of the LODs and LOQs were obtained because data were available for only two matrix blank samples.

For individual (*i.e.*, chemical by chemical) LODs and LOQs, refer to Attachment I (Checklist). The reviewer-estimated LODs for the influent wastewater samples ranged from 1.9 ng/L for cyfluthrin to 34 ng/L for permethrin and the LOQs ranged from 3.5 ng/L for cyfluthrin to 45 ng/L for permethrin. The reviewer estimates of the LODs for the effluent samples were from 'unable to calculate' (due to reported as non-detects) to 0.7 ng/L for permethrin and for the LOQs ranged from 'unable to calculate' to 1.6 ng/L for permethrin and bifenthrin. These LODs and LOQs are based upon only two matrix control samples measured.

In contrast, the registrant-claimed values for the LODs and LOQs were set arbitrarily. The claimed LODs for the influent samples were set to ⅓ of the LOQ and ranged from 1.7-17 ng/L and the LOQ ranged from 5-50 ng/L. Meanwhile, the registrant-claimed LODs for the effluent samples were also set to ⅓ of the LOQ and ranged from 0.17-1.7 ng/L and the LOQ ranged from 0.5-5.0 ng/L.

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

This method is considered unacceptable. It was validated by the same laboratory that developed the method and the author of the method was also the Laboratory Director. An independent validation was not completed and only one set of performance data was submitted. The LOQs and LODs were determined arbitrarily. Samples were analyzed at the registrant-set LOQ (while some samples were tested at a multiple above the LOQ), and 100 LOQ (it is recommended that the samples be tested at 10 LOQ). Furthermore, only three samples were tested at 100 LOQ (it is recommended that five samples be tested). Since it is not possible to obtain matrix control samples completely free of pesticides and because only two control matrix samples were tested, the reviewer-estimated LODs and LOQs are highly uncertain.

These deficiencies are considered major and the method provides only limited useful information and may not be upgraded by the submission of additional data. The registrant should provide a method with an independent laboratory validation. Furthermore, justification for the LOD and LOQ values and comparison to relevant or expected concentrations for influent samples should be provided. For the effluent samples, the LOC and LOD values should be relevant relative to environmental concentration levels, and compared to endpoints such as those obtained from ecological effects studies (*i.e.*, LC_{50}s or NOAECs times their respective LOCs).

COMPLIANCE

Signed and dated Data Confidentiality and Quality Assurance statements were not provided. A signed Approvals page was provided (p. 2).

A. BACKGROUND INFORMATION

Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin are synthetic pyrethroid insecticides subject to EPA's Registration Review (refer to http://www.epa.gov/oppsrrd1/reevaluation/pyrethroids-pyrethrins.html accessed 10/05/2011) and to CDPR's Reevaluation (refer to http://www.cdpr.ca.gov/docs/registration/reevaluation/chemicals/pyrethroids.htm accessed 10/05/2011). Pyrethroids may be used in multiple products both in agricultural

and non-agricultural (*i.e.*, urban) settings. The primary biological effects of pyrethroids on insects and vertebrates reflect an inhibition of the correct firing of neurotransmitter deliver signals from one cell to another via nerve membrane inhibition of the voltage gated Ca^{2+} channels (calcium ion channels), coupled with a stimulatory effect on the voltage gated Na^{+} channels (sodium ion channels). Relative to physiological responses, researchers have designated two types of pyrethroids, Type I (*e.g.*, bifenthrin and permethrin) and Type II (*e.g.*, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin and *lambda*-cyhalothrin). Structurally, Type I pyrethroids lack the cyano-group that characterizes Type II pyrethroids.

TABLE A.1. Test Compound Nomenclature	
Parameter	**Value**
Common name	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin
Company experimental name	Not reported
IUPAC name	For chemical names, lot numbers, CAS #'s and structures see the Attachment II. Sources of test compounds, purities, lot numbers, expiration dates, and storage conditions are also shown in the Attachment II.
CAS Name	
CAS #	
Structure	

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound	
Parameter	**Value**
Melting point/range (°C)	These properties were not provided in the study report.
pH	
Density (g/cm^3)	
Water solubility at 20 °C (mg/L)	
Solvent solubility at 20 °C (mg/L)	
Vapor pressure at 20 or 25°C (torr)	
Dissociation constant (pK_a)	
Octanol/water partition coefficient	
UV/visible absorption spectrum (nm)	

B. MATERIALS AND METHODS

B.1. Principle of Method

TABLE B.1. Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied	
Parameter	**Value**
Method ID	Meth-201 using GC-MS NCI
Analyte(s)	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin
Extraction solvent/ technique	Hexane (25 mL) is added to 500 mL samples and procedure is followed or they are stored frozen (and thawed prior to conduct of study). Methanol (50 mL) and hexane (25 mL) are added to samples, then they are vigorously shaken for one minute and allowed to partition for ~10 minutes. Then hexane (50 mL) is added to the extracted sample and partitioned in a similar way. The hexane layers are passed through sodium sulfate (20 g), the sodium sulfate is rinsed with 10 mL hexane. The hexane sample is concentrated to ~0.2 mL using a Turbo-Vap evaporator at ≤40°C, then dried with manual nitrogen blowdown, and re-dissolved in 2.0 mL hexane.
Cleanup strategies	The hexane sample is passed through a conditioned Varian Silica Bond Elut™ SPE cartridge (500 mg, 3 mL size), washed with 1 mL hexane, analytes eluted with 6 mL hexane:diethyl ether (9:1, v/v) into a test tube (13 x 100 mm). The eluate is evaporated to dryness under a stream of nitrogen using an N-Evap evaporator set to ≤40°C, redissolved in 0.5 mL (effluent) or 5.0 mL (influent) of 0.1% peanut oil in acetone solution and sonicated.
Instrument/Detector	Agilent 6890 GC with an Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode (NCI), a HP 7683 autosampler, controlled by a HP G1701CA MS ChemStation, a column type 30 x 0.25 mm i.d. fused silica column cross-bonded with 0.25 µm film thickness Varian CP-Sil 8CB-MS (Varian Corporation), and GC inlet liner 4 mm i.d. gooseneck splitless liner packed with Carbo Frit™ (Restek), carrier gas helium, injection volume 4 µL, column flow 0.9 mL/min, gradient temperature as specified in the document, ranging from 80 to 305°C. Target ions and qualifiers, and retention times as shown in the document.

C. RESULTS AND DISCUSSION

C.1. Recovery Results Summary

TABLE C.1.a. Recovery Results from Method Validation of Influent			
Analyte	**Spiking Levels (ng/L)**	**Mean Recoveries Obtained (%)**	**Relative Standard Deviation**
Bifenthrin	5	80.5	5.6
Cyfluthrin	5	102.1	9.6
Cypermethrin	50	81.2	7.8
Deltamethrin	10	99.5	7.8
Esfenvalerate	5	84.2	5.6

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TABLE C.1.a. Recovery Results from Method Validation of Influent

Analyte	Spiking Levels (ng/L)	Mean Recoveries Obtained (%)	Relative Standard Deviation
Fenpropathrin	5	76.2	6.2
Lambda-cyhalothrin	5	95.3	2.7
Permethrin	50	86.9	5.9
Bifenthrin	500	82.2	1.4
Cyfluthrin	500	97.2	1.3
Cypermethrin	500	85.4	1.8
Deltamethrin	1,000	94.3	3.1
Esfenvalerate	500	93.0	2.8
Fenpropathrin	500	97.9	1.2
Lambda-cyhalothrin	500	96.2	0.1
Permethrin	5,000	83.2	1.2

TABLE C.1.b. Recovery Results from Method Validation of Effluent

Analyte	Spiking Levels (ng/L)	Mean Recoveries Obtained (%)	Relative Standard Deviation (%)
Bifenthrin	0.5	101.0	10
Cyfluthrin	0.5	107.6	6.0
Cypermethrin	0.5	93.4	8.3
Deltamethrin	1.0	90.8	7.3
Esfenvalerate	0.5	102.1	7.2
Fenpropathrin	0.5	106.7	6.1
Lambda-cyhalothrin	0.5	107.0	8.3
Permethrin	5.0	108.7	4.3
Bifenthrin	50	89.1	5.7
Cyfluthrin	50	105.9	3.6
Cypermethrin	50	93.8	5.7
Deltamethrin	100	93.4	6.1
Esfenvalerate	50	97.8	7.0
Fenpropathrin	50	101.8	2.0
Lambda-cyhalothrin	50	103.1	3.4
Permethrin	500	94.3	6.2

C.1.1. Method Characteristics

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TABLE C.2. Method Characteristics

Parameter	**Value**		
Analytes	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin		
	Chemical\Sample	**Influent**	**Effluent**
Limit of Quantitation (**LOQ**)	Bifenthrin	3.9	1.6
[Reviewer's estimate]	Cypermethrin	3.5	ND in controls
	Cyfluthrin	4.7	0.04
	Deltamethrin	15	0.08
	Esfenvalerate	3.8	0.1
	Fenpropathrin	4.5	ND in controls
	Lambda-cyhalothrin	26	1.2
	Permethrin	45	1.6
Limit of Detection (**LOD**)	Bifenthrin	2.9	0.07
[Reviewer's estimate]	Cypermethrin	1.9	ND in controls
	Cyfluthrin	3.5	0.6
	Deltamethrin	2.1	0.03
	Esfenvalerate	5.6	0.04
	Fenpropathrin	2.3	0.07
	Lambda-cyhalothrin	3.8	ND in controls
	Permethrin	34	0.7
Accuracy/Precision at LOQ	At the LOQ average recoveries were within the range 76-109% and the relative standard deviations were within ND-10%.		
Reliability of the Method/[ILV]	Not applicable, no ILV conducted		
Linearity	For all analytes and according to reported data, $r^2 \geq 0.999$.		
Specificity	GC/MS – NCI appeared to be specific for the analytes based on inspection of the sample gas chromatographs. For six of the eight analytes there were 2 or 4 peaks. The response for the chemical was the sum total of all peaks.		
ND = Not Detected			

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

C.2. Independent Laboratory Validation (ILV)

No ILV was conducted.

TABLE C.3.a. Recovery Results of the Method Obtained by an Independent Laboratory Validation for the Determination of Residues in Influent Wastewaters

Analyte	Spiking Level (units)	Mean Recoveries Obtained (%)	Relative Standard Deviation (%)
Bifenthrin	Not available, no true ILV was provided.		
Cypermethrin			
Cyfluthrin			
Deltamethrin			
Esfenvalerate			
Fenpropathrin			
Lambda-cyhalothrin			
Permethrin			

TABLE C.3.b. Recovery Results of the Method Obtained by an Independent Laboratory Validation for the Determination of Residues in Effluent Wastewaters

Analyte	Spiking Level (units)	Mean Recoveries Obtained (%)	Relative Standard Deviation (%)
Bifenthrin	Not available, no true ILV was provided.		
Cypermethrin			
Cyfluthrin			
Deltamethrin			
Esfenvalerate			
Fenpropathrin			
Lambda-cyhalothrin			
Permethrin			

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D. CONCLUSION

The method was performed by the same laboratory that developed the method but an independent validation was not completed. The LOQs and LODs were determined arbitrarily. It is recommended that five samples be tested at the LOQ and at 10 LOQ. In this study, samples were analyzed at the LOQ (some samples were tested at a value above the LOQ due to interferences), and at 100 LOQ. Only three samples were tested at 100 LOQ. Since it is not possible to obtain control matrix samples completely free of pesticides and because only two control matrix samples were tested, the estimated LODs and LOQs are highly uncertain. No interferences were reported.

These deficiencies are considered major and the method provides only limited useful information and may not be upgraded by the submission of additional data. The registrant should provide a method with an independent laboratory validation, justify the LOD and LOQ calculated values and compare them to relevant environmental concentrations or endpoints, such as those obtained from ecological effects studies (*e.g.*, LC_{50}s or NOAECs times their LOCs), particularly for the effluent samples.

There are two attachments to this review: Attachment I. Environmental Chemistry Method Review Checklist, and Attachment II. Names, chemical names, CAS numbers, structures, percent purities, lot numbers, sources and structures for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

Attachment I:

**ENVIRONMENTAL CHEMISTRY METHOD (ECM)
STANDARD EVALUATION PROCEDURE (SEP) CHECKLIST:
BACKGROUND AND INITIAL REVIEW INFORMATION**

"Determination of residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in **Wastewater (Influent and Effluent)**, Dated September 30, 2010. Validation Report." (MRID 48638501)

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

I. Background Information

A.	**Title of Method**	Validation of Morse Laboratories, LLC Analytical Method (METH-201): "Determination of residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater (Influent and Effluent), Dated September 30, 2010. Validation Report." Morse Labs Project No.: ML10-1602-PWG. Meth-201. Date of the Report December 3, 2010. Performed by Morse Laboratories, LLC, and Submitted by Pyrethroid Working Group, 200 pp. Author: J.M. Willoh
B.	**ECM No.** [For BEAD]	
C.	**MRID No.**	48638501
D.	**Matrix**	Influent and effluent wastewaters from POTWs
E.	**Analytes detected**	All analytes are parent synthetic pyrethroid insecticides: bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin. For structures, CAS Reg. No., CAS names, IUPAC names and structures, refer to the Attachment II.

II. Information about the Laboratory

A.	**Name**	Morse Laboratories, LLC
B.	**Address**	1525 Fulton Avenue Sacramento, CA 95825
C.	**Telephone No.**	Not provided
D.	**Name of the Study Director**	Jeri M. Willoh, Analytical Project Coordinator
E.	**Name of the Lead Chemist**	Kevin Clark, Laboratory Director
F.	**Laboratory Validation:**	Kevin Clark, Method Author

III. Method Summary Information for Analytes:

Samples were taken from a publicly owned treatment works (POTW) in Suffern, NY. Influent samples were collected after bar screening and a comminutor (*i.e.*, a machine that pulverizes solids), but prior to grit removal. These procedures remove large objects from the wastewater. Effluent samples were collected after primary settling, trickling filter biological treatment with secondary clarification, activated sludge biological treatment, final settling through integral clarifiers and ultraviolet disinfection. This is an analytical method used for the determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in influent and effluent wastewater samples.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

A.	**Statement of Data Confidentiality**	No. The method does not provide a statement regarding data confidentiality. This method was submitted to CDPR under California Notice 2006-13.
1.	**Is the Method Classified or Confidential?**	No statement claiming confidentiality was provided.
2.	**Submitted Prior to 2008 with a Non-Standard Claim of Confidentiality?**	No.
B.	**Sample Preparation**	"Upon receipt of the samples at the laboratory, they were immediately placed in refrigerated storage (typically 1-8 °C), where they remained pending sub sampling and analysis." No further sample preparation was required.
C.	**Sample Extraction**	Hexane (25 mL) is added to 500 mL samples and procedure is followed or they are stored frozen (and thawed prior to conduct of study). Methanol (50 mL) and additional hexane (25 mL) are added to samples, then they are vigorously shaken for one minute and allowed to partition for ~10 minutes in a separatory funnel. Then hexane (50 mL) is added to the extracted sample and partitioned in a similar way. The hexane layers are passed through sodium sulfate (20 g), the sodium sulfate is rinsed with 10 mL hexane. The hexane sample is concentrated to ~0.2 mL using a Turbo-Vap evaporator at $\leq 40^{0}$C, then dried with manual nitrogen blowdown, and re-dissolved in 2.0 mL hexane.
D.	**Sample Cleanup**	The hexane sample is passed through a conditioned Varian Silica Bond Elut™ SPE cartridge (500 mg, 3 mL size), washed with 1 mL hexane, analytes eluted with 6 mL hexane:diethyl ether (9:1, v/v) into a test tube (13 x 100 mm). The eluate is evaporated to dryness under a stream of nitrogen using an N-Evap evaporator set to $\leq 40^{0}$C, redissolved in 0.5 mL (effluent) or 5.0 mL (influent) of 0.1% peanut oil in acetone solution and sonicated.
E.	**Sample Derivatization**	Not applicable to this procedure.
F.	**Sample Analysis**	Residues determined using GC-MS/NCI
1.	**Instrumentation**	Agilent 6890 GC with an Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode (NCI), a HP 7683 autosampler, controlled by a HP G1701CA MS ChemStation, and GC inlet liner 4 mm i.d. gooseneck splitless liner packed with Carbo Frit™ (Restek), carrier gas helium, injection volume 4 µL, column flow 0.9 mL/min, gradient temperature as specified in the document, ranging from 80 to 305^{0}C.
2.	**Primary Column**	30 m× 0.25 mm i.d. fused silica column cross-bonded with 0.25 µm film thickness Varian CP-Sil 8CB-MS (Varian Corporation)
3.	**Confirmatory Column**	MS considered a confirmatory technique.
4.	**Detector**	Agilent 5973N mass selective detector (MS) operated in negative chemical ionization mode (NCI).

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5.	**Other Confirmatory Techniques**	Target ions and qualifier ions, and retention times as shown in the document.		
6.	**Other Relevant Information**	All the analytes except for bifenthrin and fenpropathrin show more than one peak in GC. When making calculations, this was considered by calculating the total peak response (total of all isomer responses/ chemical).		
G.	**Detection and Quantitation Limits**			
1.	**Limit of Quantitation (LOQ)**	***Reviewer-estimated based on only two matrix "blanks"**		
	Influent Wastewater Samples	**Claimed in Method**	**Estimated***	
	Bifenthrin	5 ng/L	3.9 ng/L	
	Cyfluthrin	5 ng/L	3.5 ng/L	
	Esfenvalerate	5 ng/L	4.7 ng/L	
	Fenpropathrin	5 ng/L	15 ng/L	
	Lambda-cyhalothrin	5 ng/L	3.8 ng/L	
	Deltamethrin	10 ng/L	4.5 ng/L	
	Cypermethrin	50 ng/L	26 ng/L	
	Permethrin	50 ng/L	45 ng/L	
	Effluent Wastewater Samples	**Claimed in Method**	**Estimated***	
	Bifenthrin	0.5 ng/L	1.6 ng/L	
	Cyfluthrin	0.5 ng/L	Reported not detected in controls	
	Esfenvalerate	0.5 ng/L	0.04 ng/L	
	Fenpropathrin	0.5 ng/L	0.08 ng/L	
	Lambda-cyhalothrin	0.5 ng/L	0.1 ng/L	
	Deltamethrin	1.0 ng/L	Reported not detected in controls	
	Cypermethrin	5.0 ng/L	1.2 ng/L	
	Permethrin	5.0 ng/L	1.6 ng/L	
2.	**Limit of Detection (LOD)**	***Reviewer-estimated based on only two matrix "blanks"**		
	Influent Wastewater Samples	**Claimed (⅓ LOQ)**	**Estimated***	
	Bifenthrin	1.7 ng/L	2.9 ng/L	
	Cyfluthrin	1.7 ng/L	1.9 ng/L	
	Cypermethrin	1.7 ng/L	3.5 ng/L	
	Esfenvalerate	1.7 ng/L	2.1 ng/L	
	Fenpropathrin	1.7 ng/L	5.6 ng/L	
	Lambda-cyhalothrin	1.7 ng/L	2.3 ng/L	
	Deltamethrin	3.3 ng/L	3.8 ng/L	
	Permethrin	17 ng/L	34 ng/L	
	Effluent Wastewater Samples	**Claimed (⅓ LOQ)**	**Estimated***	
	Bifenthrin	0.17 ng/L	0.07 ng/L	
	Cyfluthrin	0.17 ng/L	Reported not detected in controls	
	Cypermethrin	0.17 ng/L	0.6 ng/L	
	Esfenvalerate	0.17 ng/L	0.03 ng/L	
	Fenpropathrin	0.17 ng/L	0.04 ng/L	

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	Lambda-cyhalothrin	0.17 ng/L	0.07 ng/L	
	Deltamethrin	0.33 ng/L	Reported not detected in controls	
	Permethrin	1.7 ng/L	0.7 ng/L	

H. Recovery (Accuracy) /Precision Data

Influent Wastewater Samples

	At LOQ (%) [1]				At 100 LOQ (%) [1]			
	Range	**Mean**	**SD**	**RSD**	**Range**	**Mean**	**SD**	**RSD**
Bifenthrin	75-85 [2]	80.5	4.7	5.6	81-84	82.2	1.1	1.4
Cyfluthrin	93-116 [3]	102.1	9.8	9.6	96-99	97.2	1.3	1.3
Cypermethrin	73-89	81.2	5.9	7.8	85-87	85.4	1.5	1.8
Deltamethrin	91-107	99.5	7.8	7.8	91-96	94.3	2.9	3.1
Esfenvalerate	79-89	84.2	4.7	5.6	90-95	93.0	2.7	2.8
Fenpropathrin	72-81 [4]	76.2	4.7	6.2	96-99	97.9	1.2	1.2
Lambda-cyhalothrin	93-99 [5]	95.3	2.6	2.7	96-96	96.2	0.1	0.1
Permethrin	82-95	86.9	5.1	5.9	82-84	83.2	1.0	1.2

1. **These recoveries are based upon an arbitrary LOQ that was set by the registrant. At the LOQ, five samples were tested while at 100 LOQ only three samples were tested. No samples were tested at 10 LOQ.** 2. One outlier at 133%. 3. One outlier at 238%. 4. One outlier at 127%. 5. One outlier at 159%. Samples were determined to be outliers per Grubbs' test.

Effluent Wastewater Samples

	At LOQ (%)[1]				At 100 LOQ (%)[1]			
	Range	**Mean**	**SD**	**RSD**	**Range**	**Mean**	**SD**	**RSD**
Bifenthrin	86-112	101.0	10.4	10.3	83-93	89.1	5.1	5.7
Cyfluthrin	102-118	107.6	6.4	6.0	102-110	105.9	3.8	3.6
Cypermethrin	86-105	93.4	7.8	8.3	89-100	93.8	5.3	5.7
Deltamethrin	84-100	90.8	6.7	7.3	88-99	93.4	5.8	6.1
Esfenvalerate	97-115	102.1	7.4	7.2	90-103	97.8	6.8	7.0
Fenpropathrin	102-117	106.7	6.5	6.1	100-104	101.8	2.1	2.0
Lambda-cyhalothrin	96-115	107.0	8.9	8.3	100-107	103.1	3.5	3.4
Permethrin	104-117	108.7	5.1	4.3	88-99	94.3	5.8	6.2

1. **These recoveries are based upon an arbitrary LOQ that was set by the registrant. At the LOQ and 100 LOQ, five and three samples were tested, respectively. No samples were tested at 10 LOQ.**

IV. Detailed Information about the Method

		YES	NO	REVIEW FURTHER
A.	**Does the method require spiking with the analytes of interest?**		X	

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		YES	NO	REVIEW FURTHER
B.	**If the method requires explosive or carcinogenic reagents, are proper precautions explained?**	Not applicable		
C.	**Is the following information supplied?**			
1.	**Detailed stepwise description of:**			
a.	**The sample preparation procedure?**	X		
b.	**The sample spiking procedure?**	X		
c.	**The extraction procedure?**	X		
d.	**The derivatization procedure?**	Not applicable		
e.	**The clean-up procedure?**	X		
f.	**The analysis procedure?**	X		
2.	**Procedures for:**			
a.	**Preparation of standards?**	X		
b.	**Calibration of instrument?**	X		
3.	**List of glassware and chemicals**	X		
a.	**Are sources recommended?**		X	
b.	**Are they commercially available?**	X		
4.	**Name, model, *etc.*, of the instrument, column, detector, *etc.*, used?**	X		
a.	**Are sources recommended?**	X		
b.	**Are they commercially available?**	X		
5.	**LOD**			
a.	**Is there an explanation of how it was calculated?**		X	
b.	**Is it a scientifically accepted procedure?**		X	
c.	**Is the matrix blank free of interferences(s) at the retention time, wavelength, *etc.*, of the analytes of interest?**		X	

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
6.	LOQ			
a.	Is there an explanation of how it was calculated?		X	
b.	Is it a scientifically accepted procedure?		X	
7.	Precision and accuracy data			
a.	Were there an adequate number of spiked samples analyzed?		X	
b.	Are the mean recoveries between 70-120%?	X		
c.	Are the RSDs of the replicates 20% or less at or above the LOQ?	X		
8.	Description and/or explanation of:			
a.	Areas where problems may be encountered?			X
b.	Critical steps?			X
c.	Interferences that may be encountered?		X	
9.	Characterization of the Matrices?		X	

V. Representative Chromatograms

		YES	NO	REVIEW FURTHER
A.	Are there representative chromatograms for:			
1.	Analytes in each matrix at the LOQ and 10 x LOQ?		X	
2.	Method blanks?	X		
3.	Matrix blanks?	X		
4.	Standard curves?	X		
a.	Do the standard curves have acceptable linearity? [$r^2 \geq 0.999$]	X		
5.	Standards that can be used to recalculate some of the values for analytes in the sample chromatograms?			X

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
B.	**Can the responses of the analytes in the chromatograms of the lowest spiking level be accurately measured?**	X		

VI. Good Laboratory Practice (GLP) Standards

		YES	NO	REVIEW FURTHER
A.	**Is there a statement of adherence to the FIFRA GLP standards?**		X	

VII. Independent Lab Validation (ILV)

		YES	NO	REVIEW FURTHER
A.	**Was an ILV performed?**		X	
B.	**Was the validation independent?**	Not applicable, ILV not performed.		
C.	**Did the ILV's precision/accuracy data meet the criteria established in OPPTS Guideline 850.6100?**	Not applicable, ILV not performed.		
D.	**Were recommendations of major or minor modifications to the method made by the independent lab performing the ILV? If major modifications were suggested, what were they?**	Not applicable, ILV not performed.		

VIII. Completeness

		YES	NO	REVIEW FURTHER
A.	**Has enough information been supplied to do a proper review?**		X	
B.	**Has enough information been supplied to do a laboratory evaluation, if requested?** [BEAD ECB determination.]			

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
C.	**Are all steps in the method scientifically sound?**	X		
D.	**Is a confirmatory method or technique provided?**	X		
E.	**Check the category below which best describes this ECM.**	**Satisfactory**	**Major Deficiencies**	**Minor Deficiencies**
1.			X	

IX. Recommendations

The analytical method was validated by the same laboratory that developed the method. The LOQs and LODs were determined arbitrarily. Samples were analyzed at the LOQ, and 100 LOQ; however, it is recommended to test at LOQ and at 10 LOQ. Furthermore, only three samples were tested at 100 LOQ (recommended five samples). Since it is not possible to obtain control matrix samples completely free of pesticides and because only two control matrix samples were tested, the estimated LODs and LOQs are highly uncertain. Registrant-reported LODs and LOQs appeared inappropriate particularly for the influent samples, based upon a comparison with the reviewer-estimated values.

These deficiencies are considered major and the method provides only limited useful information and may not be upgraded by the submission of additional data. The registrant should provide a method with an independent laboratory validation, justify the LOD/LOQ combination selected values and compare them to relevant endpoints, such as those obtained from ecological effects studies (*e.g.*, LC_{50}s and NOAECs times the LOCs), particularly for the effluent samples, and expected concentrations in influent samples.

José Luis Meléndez 10/24/2011

Primary Reviewer: José L. Meléndez, Chemist

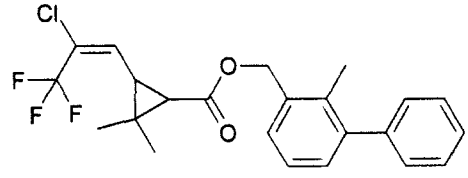
Reuben Baris 11/01/2011

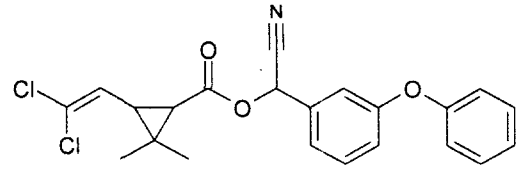
Secondary Reviewer: Reuben Baris, Environmental Scientist
EFED's Pyrethroid Review Team Representative

Attachment II:

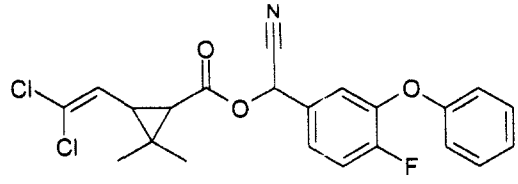
Names, chemical names, CAS numbers, structures, percent purities, lot numbers, sources and structures for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin

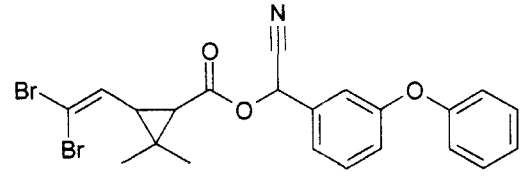
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

Compound	Bifenthrin
IUPAC Name:	2-methylbiphenyl-3-ylmethyl (*Z*)-(1*RS*,3*RS*)-3-(2-chloro-3-3-3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	82657-04-3
CAS Name:	(2-methyl[1,1'-biphenyl]-3-(2-chloro-3-3-3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	97.8
Lot No.:	BI-29
Source:	FMC Agricultural Products
Expiration Date:	8/2012
Storage:	Typically -8 °C to -22 °C

Compound	Cypermethrin
IUPAC Name:	(*RS*)-α-cyano-3-phenoxybenxyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	52315-07-8
CAS Name:	Cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	99.3
Lot No.:	479549
Source:	Syngenta Crop Protection
Expiration Date:	8/31/2011
Storage:	Typically 1 °C to 8 °C

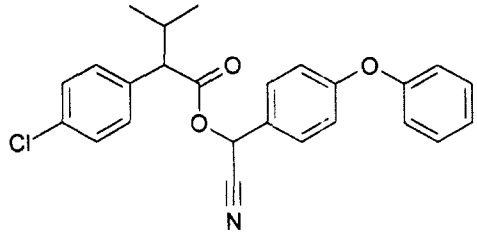
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

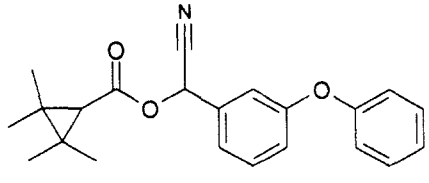
Compound	Cyfluthrin
IUPAC Name:	*(RS)*-α-cyano-4-fluoro-3-phenoxybenzyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	68359-37-5
CAS Name:	Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	98
Lot No.:	446-18A
Source:	Chem Service
Expiration Date:	04/2014
Storage:	Typically -8 °C to -22 °C

Compound	Deltamethrin
IUPAC Name:	(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	52918-63-5
CAS Name:	1-[*R*-[1-α(*S**),3α]]-cyano(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	99.5
Lot No.:	437-93B
Source:	Chem Service
Expiration Date:	02/2013
Storage:	Typically -8 °C to -22 °C

I/E

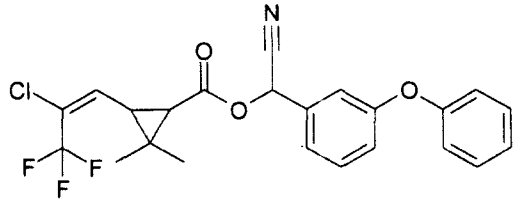
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

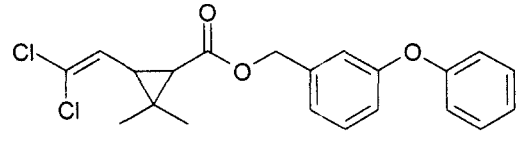
Compound	Esfenvalerate
IUPAC Name:	(*S*)-α-cyano-3-phenoxybenzyl (*S*)-2-(4-chlorophenyl)-3-methylbutyrate
CAS Number:	66230-04-4
CAS Name:	[*S*-(*R**,*R**)]-cyano(3-phenoxyphenyl)methyl 4-chloro-2-(1-methylethyl)benzeneacetate
Structure:	
% Purity:	98.7
Lot No.:	419-137B
Source:	Chem Service
Expiration Date:	03/2015
Storage:	Ambient

Compound	Fenpropathrin
IUPAC Name:	(*RS*)-α-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate
CAS Number:	64257-84-7
CAS Name:	Cyano(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate
Structure:	
% Purity:	99.5
Lot No.:	414-115A
Source:	Chem Service
Expiration Date:	12/2013
Storage:	Typically -8 °C to -22 °C

I/E

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

Compound	Lambda-cyhalothrin
IUPAC Name:	A reaction product containing equal quantities of (*S*)-α-cyano-3-phenoxybenzyl (*Z*)-(1*R*,3*R*)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (*R*)-α-cyano-3-phenoxybenzyl (*Z*)-(1*R*,3*R*)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	91465-08-6
CAS Name:	[1α(*S**),3α(*Z*)]-(±)-cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	99.5
Lot No.:	446-94A
Source:	Chem Service
Expiration Date:	5/2014
Storage:	Typically 1 °C to 8 °C

Compound	Permethrin
IUPAC Name:	3-phenoxybenzyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
CAS Number:	52645-53-1
CAS Name:	(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Structure:	
% Purity:	98.0
Lot No.:	401-113A
Source:	Chem Service
Expiration Date:	04/2011
Storage:	Typically 1 °C to 8 °C

I/E

MRID 48638501

Reviewer-Estimated LODs and LOQs for Influent and Effluent, from Two Matrix "Blank" Samples

					Est. LOD	Est. LOQ
	Influent Matrix "Blanks" (ng/L)		Mean	SD	Mean + 3SD	Mean + 10 SD
Bifenthrin	2.38	2.58	2.48	0.141421356	2.9	3.9
Cyfluthrin	1.67	1.54	1.605	0.091923882	1.9	2.5
cypermethrin	14.7	16.2	15.45	1.060660172	18.6	26.1
deltamethrin	3.56	3.42	3.49	0.098994949	3.8	4.5
esfenvalerate	1.32	0.799	1.0595	0.368402633	2.2	4.7
fenpropathrin	0.639	2.55	1.5945	1.351281059	5.6	15.1
lambda-cyhalothrin	1.51	1.81	1.66	0.212132034	2.3	3.8
permethrin	27.6	29.9	28.75	1.626345597	33.6	45.0

	Effluent Matrix "Blanks" (ng/L)		Mean	SD	Mean + 3SD	Mean + 10 SD
Bifenthrin	0.179	0.369	0.274	0.134350288	0.7	1.6
Cyfluthrin	ND	ND	ND	ND	ND	ND
cypermethrin	0.22	0.348	0.284	0.090509668	0.6	1.2
deltamethrin	ND	ND	ND	ND	ND	ND
esfenvalerate	0.0209	0.024	0.02245	0.002192031	0.0	0.0
fenpropathrin	0.023	0.0289	0.02595	0.00417193	0.0	0.1
lambda-cyhalothrin	0.0562	0.063	0.0596	0.004808326	0.1	0.1
permethrin	0.263	0.435	0.349	0.121622366	0.7	1.6

Data were obtained from Tables 1 & 2 of study report, pp. 30-33

Influent Samples Results

MRID 48638501 Data were obtained from Table 1 of study report, pp. 30-31

Bolded values were considered outliers by the registrant as per Grubb's test; however, no further information was provided.

	Bifenthrin	Cyfluthrin	Cypermethrin	Deltamethrin	Esfenvalerate	Fenpropathrin	l-cyhalothrin	Permethrin
Influent Controls	2.48	1.61	15.45	3.49	1.06	1.59	1.66	28.75
ng/L found in influent spls.	9.11	13.50	52.10	12.60	5.52	7.93	9.59	69.70
	6.21	6.28	54.40	13.80	5.10	5.20	6.37	71.40
	6.58	7.41	59.80	14.00	5.52	5.62	6.60	76.50
	6.74	6.53	57.30	14.20	5.19	5.20	6.42	71.70
	6.48	6.61	56.70	12.60	5.02	5.60	6.30	71.70
ng/L corrected for control	6.63	11.90	36.65	9.11	4.46	6.34	7.93	40.95
	3.73	4.68	38.95	10.31	4.04	3.61	4.71	42.65
	4.10	5.81	44.35	10.51	4.46	4.03	4.94	47.75
	4.26	4.93	41.85	10.71	4.13	3.61	4.76	42.95
	4.00	5.01	41.25	9.11	3.96	4.01	4.64	42.95
ng/L fortification level	5	5	50	10	5	5	5	50
Percent recovered	**133**	**238**	73	91	89	**127**	**159**	82
	75	94	78	103	81	72	94	85
	82	116	89	105	89	81	99	96
	85	99	84	107	83	72	95	86
	80	100	83	91	79	80	93	86
Mean	80.5	102.1	81.2	99.5	84.2	76.2	95.3	86.9
Standard deviation	4.4	9.8	5.9	7.8	4.7	4.7	2.6	5.1
Relative standard deviation	5.5	9.6	7.2	7.8	5.6	6.2	2.7	5.9
Influent Controls								
ng/L found in influent spls.	420	495	451	962	475	495	483	4241
	412	484	438	962	453	484	482	4209
	409	484	438	916	470	494	483	4140

ng/L corrected for control	418	493	436	959	474	493	481	4212
	410	482	423	959	452	482	480	4180
	407	482	423	913	469	492	481	4111
ng/L fortification level	500	500	500	1000	500	500	500	5000
Percent recovered	84	99	87	96	95	99	96	84
	82	96	85	96	90	96	96	84
	81	96	85	91	94	98	96	82
Mean	82.2	97.2	85.4	94.3	93.0	97.9	96.2	83.4
Standard deviation	1.1	1.3	1.5	2.7	2.3	1.2	0.1	1.0
Relative standard deviation	1.4	1.3	1.8	2.8	2.5	1.2	0.1	1.2

Effluent Samples Results
MRID 48638501

Data were obtained from Table 2 of study report, pp. 32-33

	Bifenthrin	Cyfluthrin	Cypermethrin	Deltamethrin	Esfenvalerate	Fenpropathrin	l-cyhalothrin	Permethrin
Effluent Controls	0.274	0.000	0.284	0.000	0.022	0.026	0.060	0.349
ng/L found in effluent spls.	0.747	0.512	0.712	0.849	0.510	0.539	0.556	5.80
	0.835	0.532	0.732	0.916	0.532	0.545	0.617	5.57
	0.811	0.588	0.807	1.000	0.597	0.613	0.628	6.21
	0.797	0.548	0.774	0.937	0.518	0.566	0.538	5.70
	0.706	0.509	0.729	0.838	0.508	0.534	0.634	5.63
ng/L corrected for control	0.473	0.512	0.428	0.849	0.488	0.513	0.496	5.45
	0.561	0.532	0.448	0.916	0.510	0.519	0.557	5.22
	0.537	0.588	0.523	1.000	0.575	0.587	0.568	5.86
	0.523	0.548	0.490	0.937	0.496	0.540	0.478	5.35
	0.432	0.509	0.445	0.838	0.486	0.508	0.574	5.28
ng/L fortification level	0.5	0.5	0.5	1	0.5	0.5	0.5	5
Percent recovered	95	102	86	85	98	103	99	109
	112	106	90	92	102	104	111	104
	107	118	105	100	115	117	114	117
	105	110	98	94	99	108	96	107
	86	102	89	84	97	102	115	106
Mean	101.0	107.6	93.4	90.8	102.1	106.7	107.0	108.7
Standard deviation	10.4	6.4	7.8	6.7	7.4	6.5	8.9	5.1
Relative standard deviation	10.3	6.0	8.3	7.3	7.2	6.1	8.3	4.7
Higher Fortification Level								
ng/L found in effluent spls.	46.6	55.0	46.6	98.7	51.6	52.1	53.5	494
	41.9	51.2	44.9	87.5	45.1	50.1	50.1	439
	46.0	52.6	50.1	95.5	50.1	50.6	51.2	483

ng/L corrected for control	46.3	55.0	46.3	98.7	51.6	52.1	53.4	494
	41.6	51.2	44.6	87.5	45.1	50.1	50.0	439
	45.7	52.6	49.8	95.5	50.1	50.6	51.1	483
ng/L fortification level	50	50	50	100	50	50	50	500
Percent recovered	93	110	93	99	103	104	107	99
	83	102	89	88	90	100	100	88
	91	105	100	96	100	101	102	97
Mean	89.1	105.9	93.8	93.9	97.8	101.8	103.1	94.3
Standard deviation	5.1	3.8	5.3	5.8	6.8	2.1	3.5	5.8
Relative standard deviation	5.7	3.6	5.7	6.1	7.0	2.0	3.4	6.2

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

MEMORANDUM

DATE: November 9, 2011

SUBJECT: EFED Comments on the Pyrethroid Working Group's Environmental Chemistry Methods for Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin for the Analysis of Influent and Effluent (*i.e.*, Wastewaters), Primary Sludge and Dewatered Cake (*i.e.*, Biosolid) Samples from Publicly Owned Treatment Works
PC Codes: 128825, 109702, 128831, 097805, 109303, 127901, 128897, 109701
DP Barcode: D395988

FROM: José L. Meléndez, Chemist, ERB5
and: Pyrethroid Review Team
Environmental Fate and Effects Division (7507P)

THROUGH: Mah T. Shamim, Ph.D., Branch Chief ERB5
Pyrethroid Review Team Lead
Environmental Fate and Effects Division (7507P)

TO: Monica Wait, Chemical Review Manager
Michael Goodis, Branch Chief
Risk Management and Implementation Branch III
Pesticide Re-Evaluation Division (7508P)

The Environmental Fate & Effects Division (EFED) has reviewed two studies submitted by the Pyrethroid Working Group. The EFED evaluated all the information available and a summary of the findings is presented in **Table 1**. For details about the studies refer to the attached Data Evaluation Records (DERs).

Table 1. Environmental Fate Data Requirements for Eight Pyrethroids

Guideline Number	Data Requirement	Bibliographic Citation	Study classification
Non-guideline	Environmental Chemistry Method	48638501	Unacceptable
Non-guideline	Environmental Chemistry Method	48638601	Unacceptable

Citations for these studies are as follows:

- Willoh, J.M., 2010, "Validation of Morse Laboratories, LLC Analytical Method (METH-201): "Determination of residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater (Influent and Effluent)," Dated September 30, 2010. Morse Labs Project No.: ML10-1602-PWG. Date of the Report December 3, 2010. Unpublished study performed by Morse Laboratories, LLC, and submitted by the Pyrethroid Working Group (PWG), 200 pp. (MRID 48638501); and,

- Willoh, J.M., 2010, "Validation of the Residue Analytical Methods: 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater Treatment Primary Sludge,' Dated October 21, 2010 and 'Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin in Wastewater Treatment Dewatered Cake,' Dated October 20, 2010." Laboratory Validation of Morse Laboratories, LLC Analytical Methods Meth-204 and Meth-205. Morse Labs Project No.: ML10-1641-HQI. Date of the Report February 3, 2011. Unpublished study performed by Morse Laboratories, LLC, and submitted by the Pyrethroid Working Group, 219 pp. (MRID 48638601).

The first method referenced above is designed for the analysis of influent and effluent wastewaters from Publicly Owned Treatment Works (POTWs) while the second method is for the analysis of primary sludge and dewatered cake (*i.e.*, biosolids) from POTWs. Samples were taken from a POTW in Suffern, NY. These documents were initially submitted to the California Department of Pesticide Regulation (CDPR) as part of its directive in a letter from Ann M. Prichard, Chief of Pesticide Registration Branch, to the registrants, dated 07/15/2011. In the letter, CDPR requested "[a]cceptable analytical methods for POTW influent, effluent, and biosolids for the following eight pyrethroids: bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin, and permethrin." The Agency reviewed the studies following current "Guidance for Processing and Reviewing Environmental Chemistry Methods," dated 02/24/2011. EFED is providing the following general comments on the referenced methods.

The EPA found that these environmental chemistry methods (ECMs) do not meet the criteria for scientifically valid methods for the following main reasons:

1. According to EFED's Standard Evaluation Procedure (SEP), "Reviewing Environmental Chemistry Methods," dated 12/01/2010 and approved 02/22/2011, an initial screen of the methods was performed. EFED found during the screen that the studies were not reviewable because independent laboratory validation reports (ILVs) for the ECMs were not available. Furthermore, two complete sets of performance data were not provided for each ECM. In addition, at least five spiked samples were not analyzed at the LOQ and at 10 x LOQ. A minimum of five spiked samples should be analyzed at each concentration (*i.e.*, the LOQ and 10 x LOQ). Even though these studies were not reviewable, at CDPR's request EFED completed the review of the ECMs.
2. The LOQs and LODs were determined arbitrarily. Detection limits should not be based on arbitrarily selected lowest concentration in the spiked samples. 40 CFR Part 136, Appendix B lists some scientifically accepted procedures for estimating detection limits.

LODs are often calculated as the mean matrix blank value plus 3 times the standard deviation; LOQs are often calculated as the mean matrix blank value plus 10 times the standard deviation.

3. Since it is not possible to obtain matrix blank samples completely free of pyrethroid pesticides and because only two matrix control samples were tested, the reviewer-estimated LODs and LOQs are highly uncertain.
4. A signed and dated Data Confidentiality and Quality Assurance statements were not provided.
5. For some of the chemicals, samples were not tested at the selected LOQ. Instead, they were tested at a multiple value (*e.g.*, 2 x LOQ or 4 x LOQ), due to interferences in matrix blanks samples. Conversely, for some the chemicals, the results were reported as "not detected" in the matrix blank precluding LOD and LOQ estimation.
6. Some samples were regarded as outliers; however, no supporting statistical information was provided. It was only stated that they were outliers per Grubbs' test.

These deficiencies are considered major and the methods provide only limited useful information. The studies cannot be upgraded by the submission of additional data. The registrant should provide chemistry methods (ECMs) with independent laboratory validations (ILVs); in addition, justification for the LODs and LOQs selected should be provided. The LODs and LOQs should be compared to relevant expected concentrations for influent, effluent, primary sludge and biosolid samples, and to relevant ecological effects endpoints (*e.g.*, LC_{50}s or NOAECs times the levels of concern) for applicable samples.